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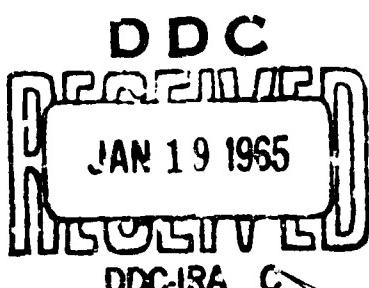
ELECTROCHEMICAL STUDIES IN THE SYNTHESIS  
OF N-F COMPOUNDS

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ARPA Order No. 399, Program Code No. 2910

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Prepared by:

Larry G. Spears

Larry D. Fiel

Wallace E. Harrell, Jr.

Margaret H. Northrup

Approved by:



Earl S. Snavely, Jr.  
Director of Chemical  
Research

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Abstract

Work during the past quarter was devoted primarily to studying the electrode reactions that occur on Monel electrodes during the electrochemical fluorination of ammonium ion in anhydrous hydrogen fluoride (AHF) and to investigating possible new electrode materials. Film resistance and cathodic stripping measurements were performed on Monel electrodes. Weight loss measurements, at open circuit and at a constant anodic potential, and anodic polarization studies were performed on Hastelloy-F, cadmium, and zinc electrodes in AHF. Both cadmium and zinc corroded rapidly in AHF, but Hastelloy-F exhibited an extremely low corrosion rate.

Several types of liquid and gas IR cells have been investigated. Calibration IR spectra were made to determine their lower limits of detection for  $\text{NF}_3(g)$ .

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I. INTRODUCTION

Monel was shown by previous work to be a satisfactory anode material for the electrochemical fluorination of nitrogen compounds in anhydrous hydrogen fluoride (AHF). Anodic polarization curves of Monel in AHF solutions of ammonium fluoride revealed no concentration-dependent plateaus to indicate a stepwise fluorination of the ammonium ion. The reproducibility of these curves was poor, however, due to a change in character of the surface film formed on Monel by anodic polarization above +4.0 volts with respect to the Hg/Hg<sub>2</sub>F<sub>2</sub> reference electrode. Cathodic stripping experiments indicated that above +4.0 v the electrode surface is covered by a persistent sorbed layer which is reduced very near the fluorine evolution potential.

During the past quarter, work on this project consisted of utilizing galvanostatic, potentiostatic, conductimetric, and spectrophotometric techniques to determine the electrode kinetics and product distribution of the electrochemical fluorination of NH<sub>4</sub>F.

## II. EXPERIMENTAL APPARATUS

There have been no major modifications in the experimental apparatus since the last quarterly report. Minor changes include the addition of a port to the electrolytic cell for syringe sampling of the evolved gases.

Liquid HF is purified routinely to a conductivity of  $10^{-5} \Omega^{-1} \text{cm}^{-1}$  by distillation and pre-electrolysis. The conductivity is determined by 1000 cycle bridge measurements using a pair of platinum disc electrodes in the experimental cell itself. The NaF trap purification step described in previous reports has been abandoned in favor of the distillation/pre-electrolysis procedure.

Samples for IR analyses were taken by flowing the cell effluent gas through a gas cell constructed of nickel and Teflon. Several materials were evaluated for use as cell windows and Irtran-2 was found to be satisfactory in regard to the chemical stability and transmission desired.

### III. ANALYTICAL WORK

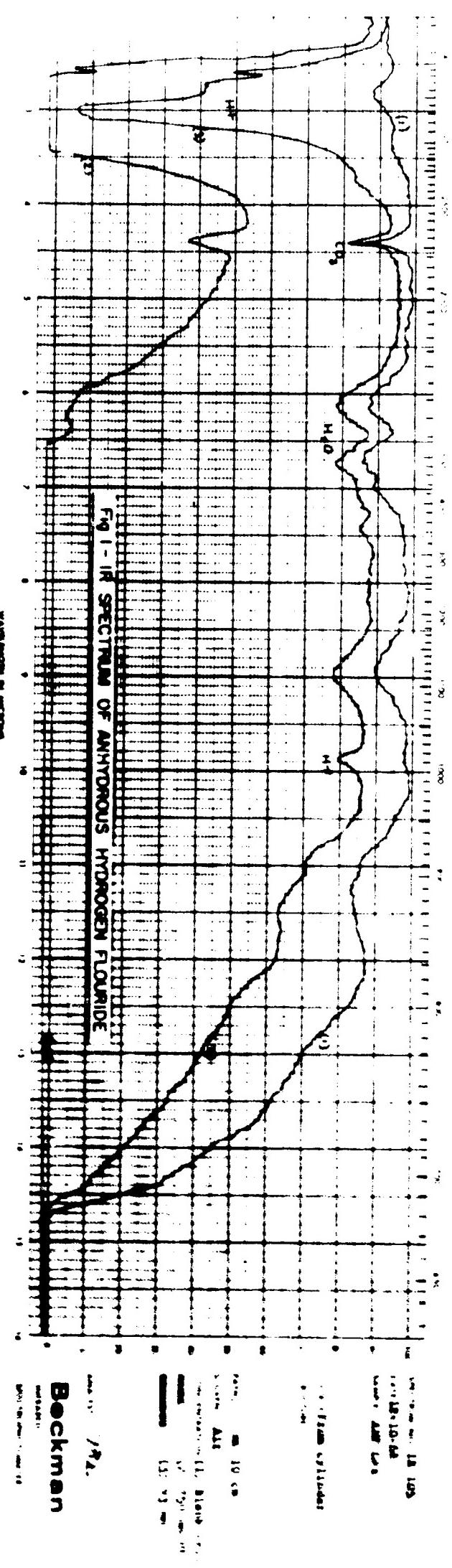
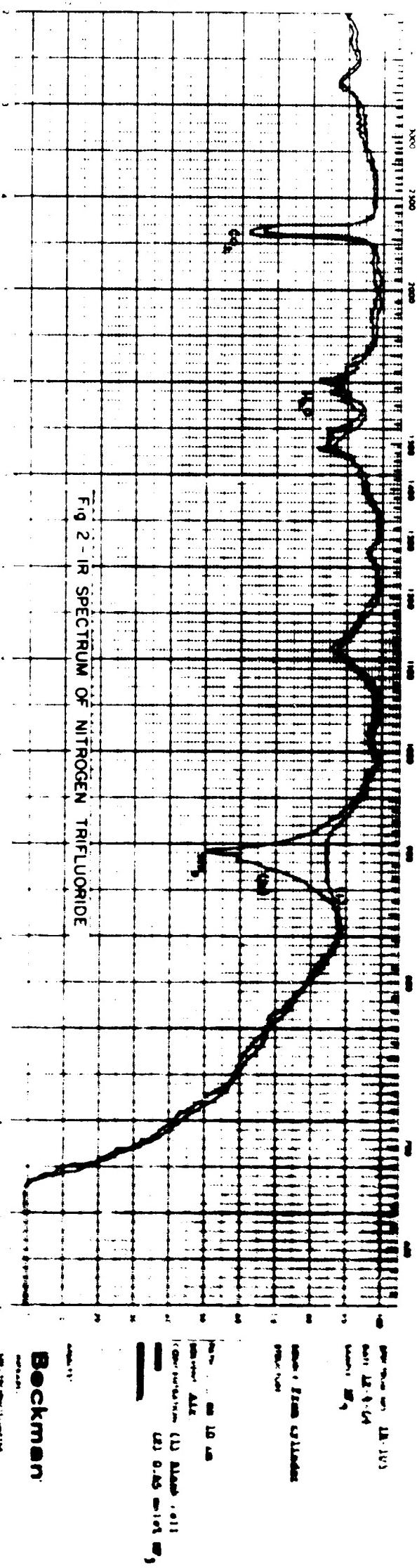
The products which may be formed by the electrochemical fluorination of ammonia in AHF include gaseous products ( $NF_3$ ,  $NHF_2$ , and  $NH_2F$ ) and soluble products ( $NHF_3^+$ ,  $NH_2F_2^+$ , etc.). A determination of the distribution of these products as a function of electrode and electrolyte parameters is necessary to describe the kinetics and mechanism of the electrode reactions. These goals are being achieved by the use of gas chromatography and infrared spectra for analyses of the vapor phase and by electrochemical measurements and infrared spectra for the solution phase. Results for the electrochemical measurements are given in later sections of this report.

The selection of materials for IR cell windows for this work is very limited because of the high reactivity of the compounds studied. From the literature it was determined that the most promising materials are Kel-F, NaCl coated with Kel-F grease,  $BaF_2$ , and Irtran-2\*. Kel-F was eliminated from consideration because its cutoff point ( $7.6\mu$ ) is too low for a study of N-F compounds (1). The use of NaCl coated with Kel-F grease was reported by Christe, *et al.*, (2); however, windows of this type are etched too rapidly by HF gas to obtain useful spectra. Barium fluoride windows are highly resistant to most chemicals including water (3). Excellent spectra for  $NF_3$  were obtained using  $BaF_2$  windows; however, the introduction of HF into the cell caused immediate fogging of the windows by a white IR-opaque film.

The most satisfactory window material found for this work is Irtran-2 (4), which gives excellent spectra for gaseous HF (Figure 1) and  $NF_3$  (Figure 2). After exposure to HF and  $NF_3$ , the background spectrum of Irtran-2 exactly reproduced the background obtained before exposure indicating a high degree of stability in the presence of fluorinated compounds. A calibration curve to be used for the analysis of  $NF_3$  in gaseous products is shown in

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\* Eastman Kodak Company, Rochester, New York.



**Beckman**  
IR SPECTROMETER

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Figure 3. The IR spectra will be combined with gas chromatograms for a complete analysis of the volatile cell products. Preliminary experiments with the chromatograph have indicated that a 20-foot long, 1/4-inch diameter Monel column packed with #40 Kel-F grease on shredded Teflon gives satisfactory results for the analysis of fluorinated mixtures.

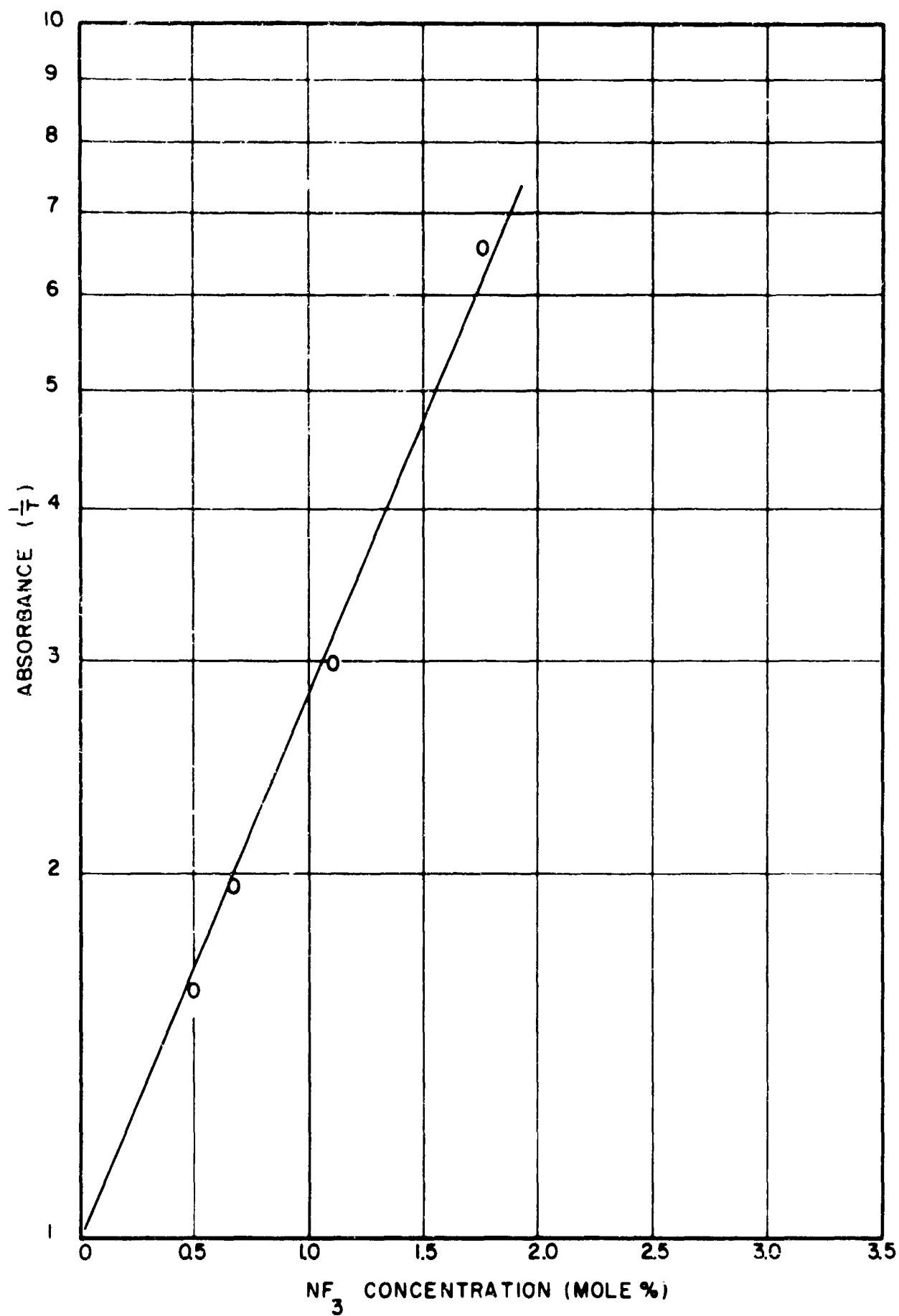


Fig. 3-ABSORBANCE OF  $\text{NF}_3$  AT  $11.02 \mu$   
IN A 10CM GAS CELL WITH  
IRTRAN-2 WINDOWS

IV. ELECTROCHEMICAL FLUORINATION OF NH<sub>4</sub>F IN ANHYDROUS HF WITH MONEL ANODES

Anodic polarization curves of Monel electrodes in AHF solutions of NH<sub>4</sub>F reported in previous quarterly reports showed an erratic behavior which was attributed to a change in the nature of the electrode surface. Various electrochemical techniques were employed during the past quarter to determine the relative distribution of products formed by the passage of anodic current. These experiments consisted of galvanostatic reduction and film resistance measurements to determine the amount and identity of corrosion product formed, conductivity measurements to determine the change in concentration of ionic species in solution, and measurements of open-circuit and forced potential decay to determine the number of reducible species formed.

Galvanostatic cathodic stripping curves of Monel electrodes polarized anodically in AHF solutions of NH<sub>4</sub>F show no significant differences to those obtained for Monel in AHF alone. In both media, potential arrests are observed on stripping if the electrode is maintained at a potential of +4.0 v (vs Hg/Hg<sub>2</sub>F<sub>2</sub>) or abcve. Stripping curves for Monel in NH<sub>4</sub>F solutions are shown in Figure 4; those for Monel in AHF were given in a previous report (Quarterly Status Report No. 6, Figure 11).

The total charge required for reduction of the film formed by anodic bias of the Monel is not reproducible when equal charges are passed at the anodic potential. As shown in Figure 5, the charge required for reduction depends on the total charge passed at +6.0 v rather than the increment of charge passed between reductions. These data are summarized in Table I. These results indicate that a portion of the film formed at +6.0 v is not reduced under the conditions employed. The arrest at +2.0 v which appears on reduction in AHF and NH<sub>4</sub>F dissolved in AHF is probably due to the reduction of fluorine which is retained in a porous film on the metal.

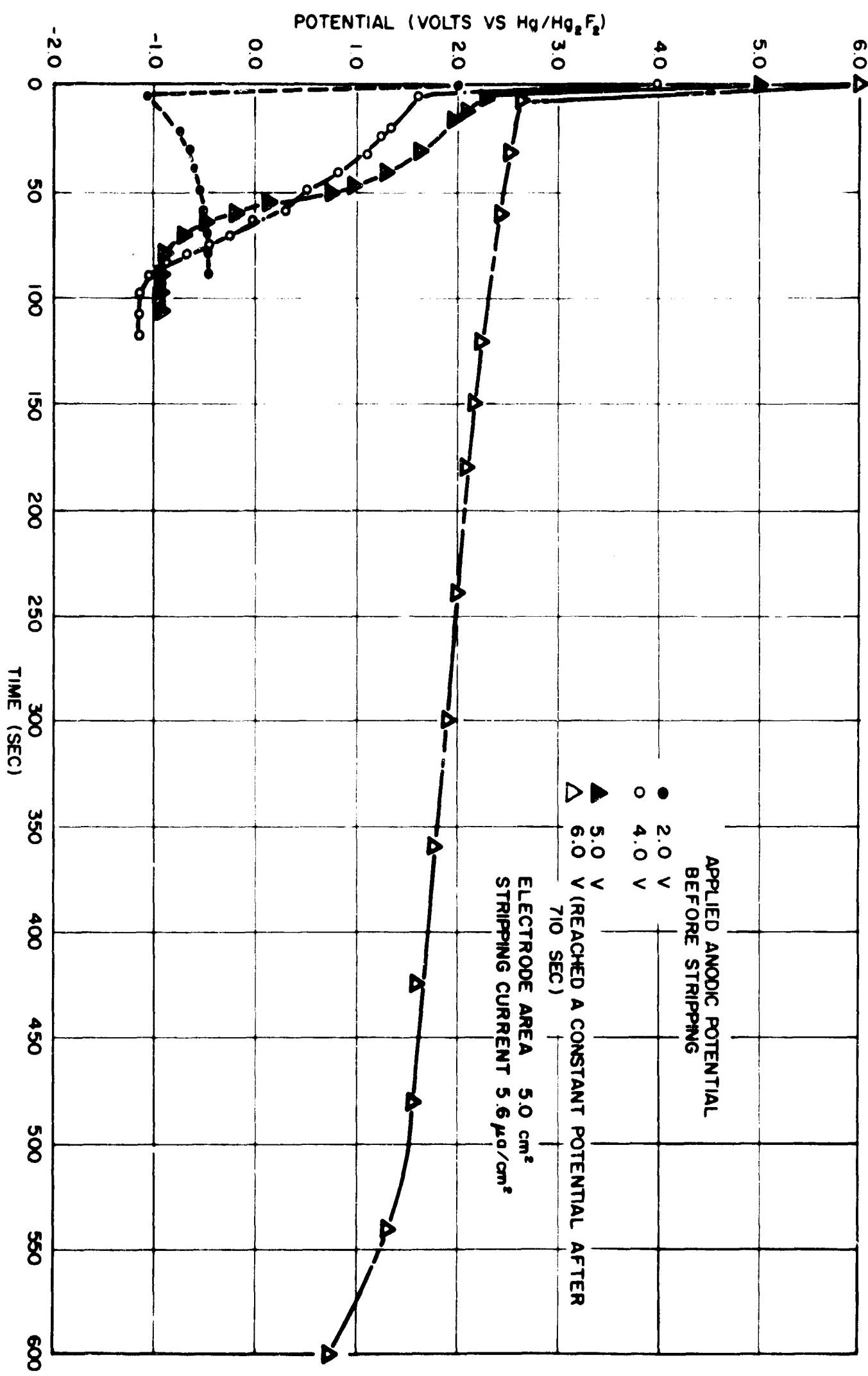


Fig. 4-STRIPPING CURVES FOR MONEL ELECTRODES POLARIZED ANODICALLY IN 0.02M NH<sub>4</sub>F IN AHF

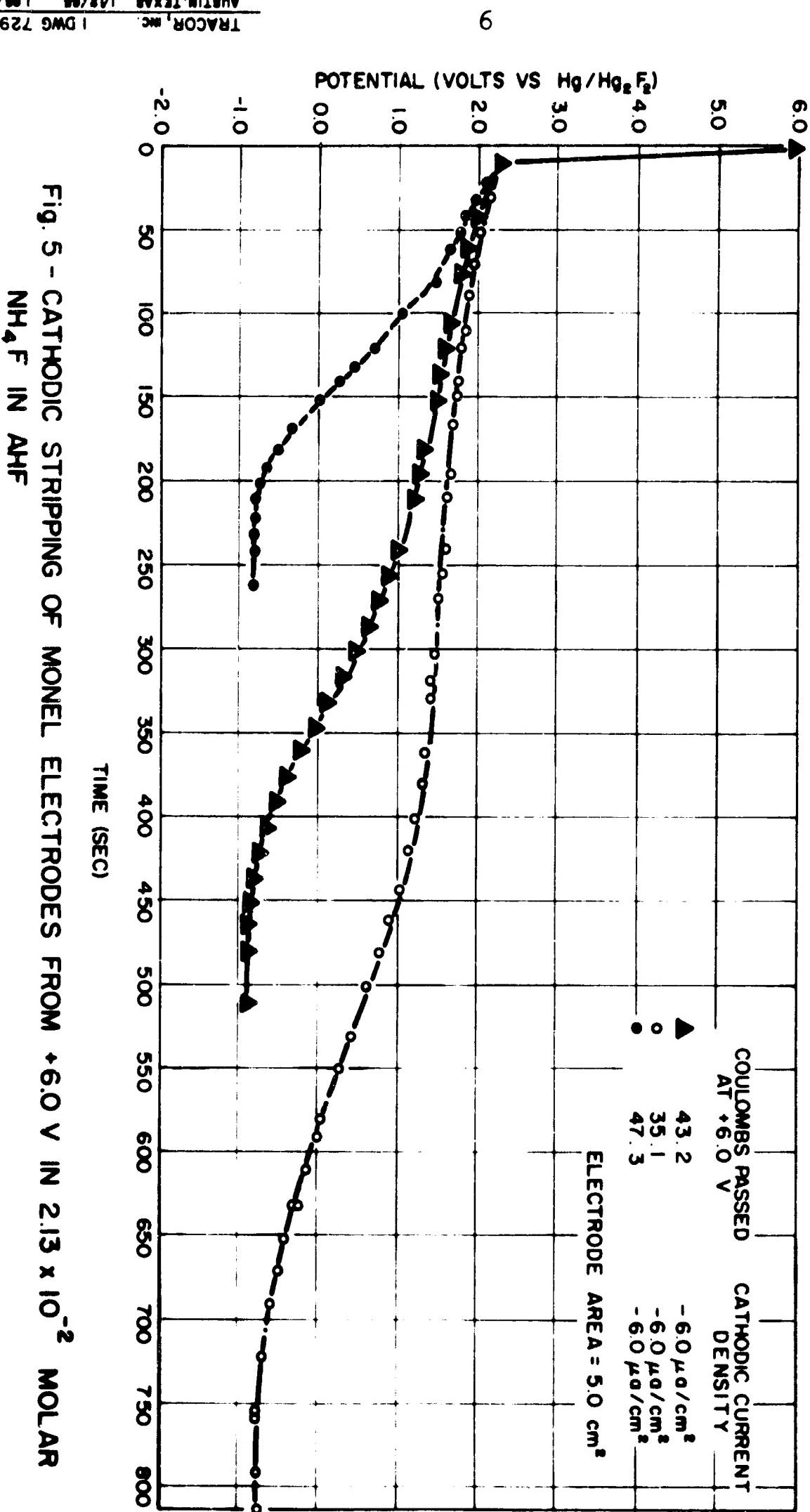


Fig. 5 - CATHODIC STRIPPING OF MONEL ELECTRODES FROM +6.0 V IN  $2.13 \times 10^{-2}$  MOLAR  $\text{NH}_4\text{F}$  IN AHF

TABLE I

CHARGE REQUIRED FOR REDUCTION OF ANODIC FILMS FORMED  
ON MONEL IN AHF SOLUTIONS OF  $\text{NH}_4\text{F}$ COULOMBS PASSED

$+6.0 \text{ v}(C_+)$	Cathodic( $C_-$ )	$(C_-/C_+) \times 10^6$	$(C_-/\Sigma C_+) \times 10^6$
47.3	$6,300 \times 10^{-6}$	133	133
43.2	$13,050 \times 10^{-6}$	302	144
35.1	$21,750 \times 10^{-6}$	619	173

Electrode film resistance measurements show a significant difference under anodic conditions and after stripping as shown in Figure 6. Film resistances were calculated from the instantaneous change in potential observed on application of a 10  $\mu\text{sec}$  constant-current, 3.6 ma pulse to the electrode. The potential changes were recorded by photographs of oscilloscope traces. Since the concentration of  $\text{NH}_4\text{F}$  employed, 0.01M, was small, the solution resistance was relatively high and therefore made a significant contribution to the measured electrode film resistance. However, the solution concentration was not changed significantly by the passage of low currents for short periods of time, so the changes observed in the film resistance on alternate anodic and cathodic treatment are believed to be accurate. As shown in Figure 6, application of cathodic current resulted in a steady decrease in film resistance, while anodic polarization to +4.0 v resulted in a rapid increase to a constant value. The average change in film resistance observed between the anodic state and stripped state was  $\pm 6.0 \Omega$  or  $30 \Omega/\text{cm}^2$ . These results and results of the cathodic stripping measurements described earlier in this report indicate that the change in film resistance is due to saturation and discharge of fluorine in the electrode corrosion product film.

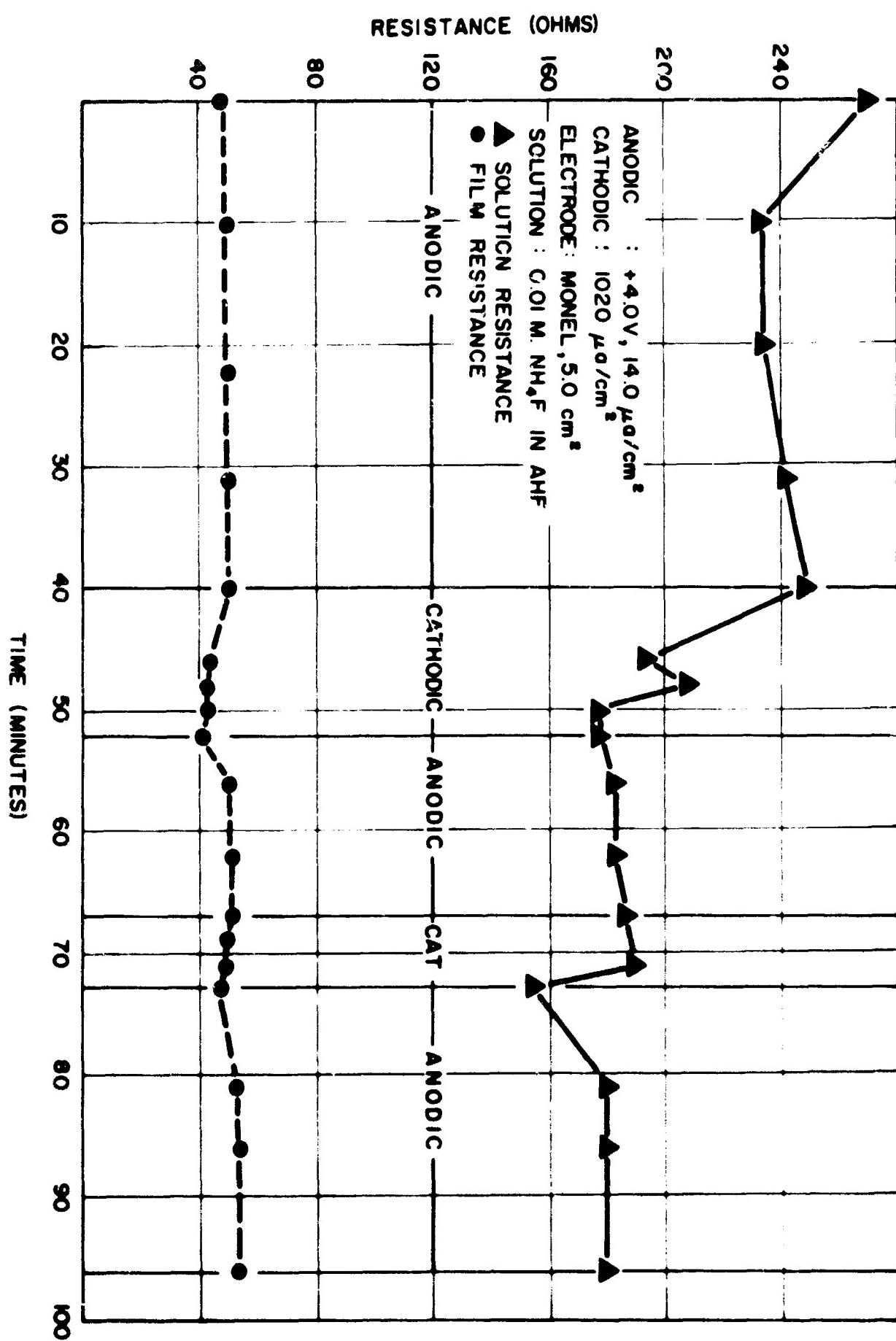


Fig. 6 - SOLUTION AND ELECTRODE FILM RESISTANCE AS A FUNCTION OF ANODIC AND CATHODIC CURRENT

V. WORKING ELECTRODES

A. Hastelloy-F

Weight loss studies were conducted on Hastelloy-F in AHF at open circuit and at a constant anodic potential. Weights were recorded (1) immediately before the electrode was introduced into the cell, (2) immediately after removal from the cell, and (3) after cleaning with hot H<sub>2</sub>O and a fiber bristle brush. The specimens usually gained weight on exposure to liquid HF. The corrosion product film was tightly adherent, insoluble in water, and was difficult to remove. As shown in Figures 7 and 8, the corrosion of Hastelloy-F is negligible at open circuit and at low anodic potentials in AHF.

At high anodic potentials (8.0 v to 10.0 v) the corrosion behavior of Hastelloy-F depends on the H<sub>2</sub>O concentration in the HF. For H<sub>2</sub>O concentrations greater than 0.05%, no appreciable corrosion is noted; but, for H<sub>2</sub>O concentrations of 0.0005% or less, Hastelloy-F has a very high corrosion rate. Several runs were made to check the corrosion current efficiency in AHF and in HF solutions with H<sub>2</sub>O or NaF added. Assuming an equivalent weight of 28 for Hastelloy-F (5), the current efficiency was found to be between 90% and 95% indicating that most of the current was used in metal dissolution.

Anodic polarization of Hastelloy-F in HF produced two distinctly different types of curves, dependent on the H<sub>2</sub>O concentration in the HF. The polarization curves shown in Figure 9 were run in HF with H<sub>2</sub>O concentrations of 0.0002% and 0.08%. The curve for 0.0002% H<sub>2</sub>O in Figure 9 shows a film buildup starting at about +5.0 v. After these runs, the electrode lost 2.28 mg/cm<sup>2</sup> and had a heavy gray-green crusty film. The electrode which was used in 0.08% H<sub>2</sub>O showed no visible signs of corrosion and no significant weight change. Evidently this additional amount of H<sub>2</sub>O in the HF inhibits corrosion of the electrode at the higher anodic potentials. This effect has been observed also by Donahue and Nevitt (6).

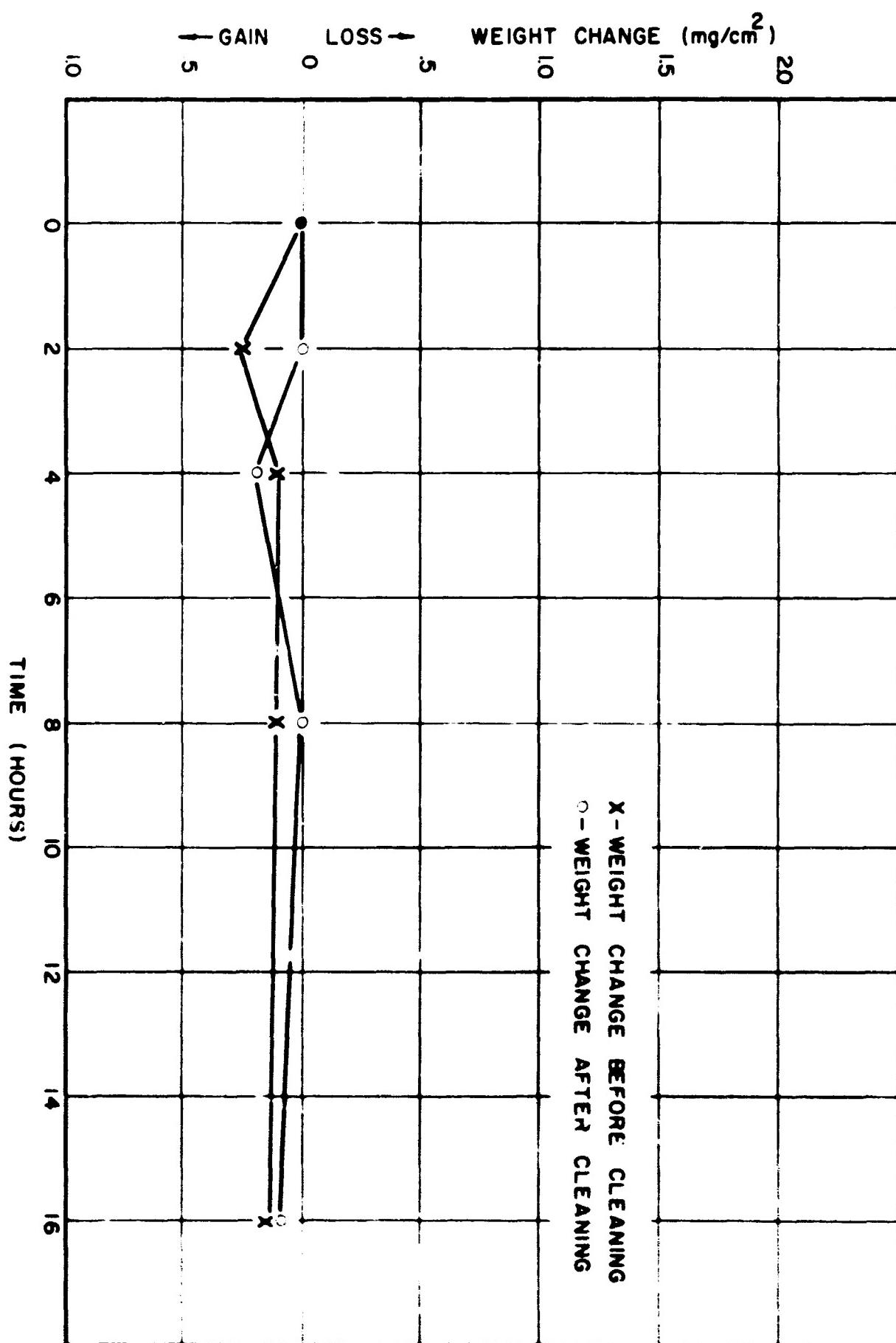


Fig.7 - WEIGHT CHANGES OF HASTELLOY-F IN AHF AT OPEN CIRCUIT

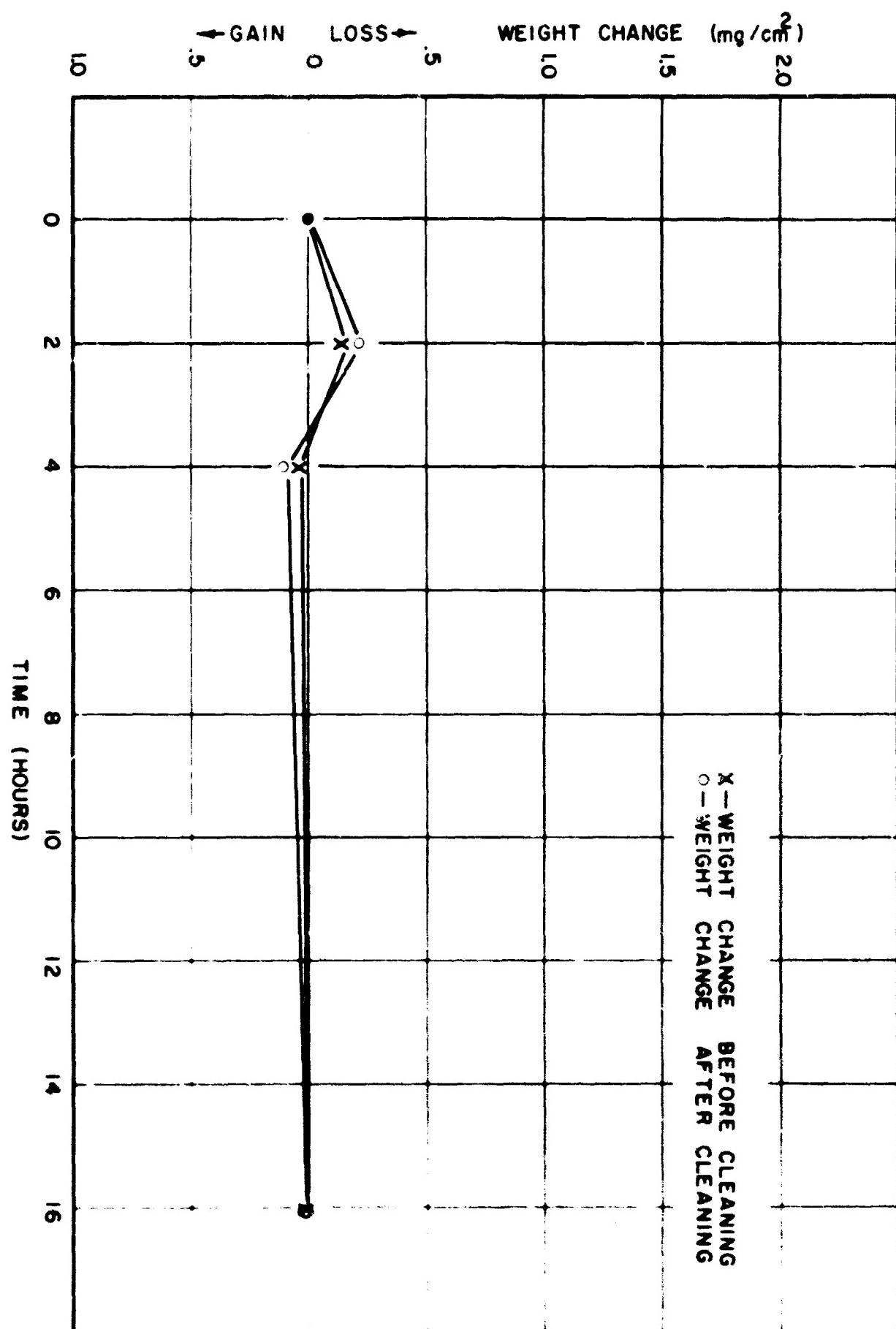


Fig. 8 - WEIGHT CHANGES OF HASTELLOY-F IN AHF  
AT +4.0 VOLTS

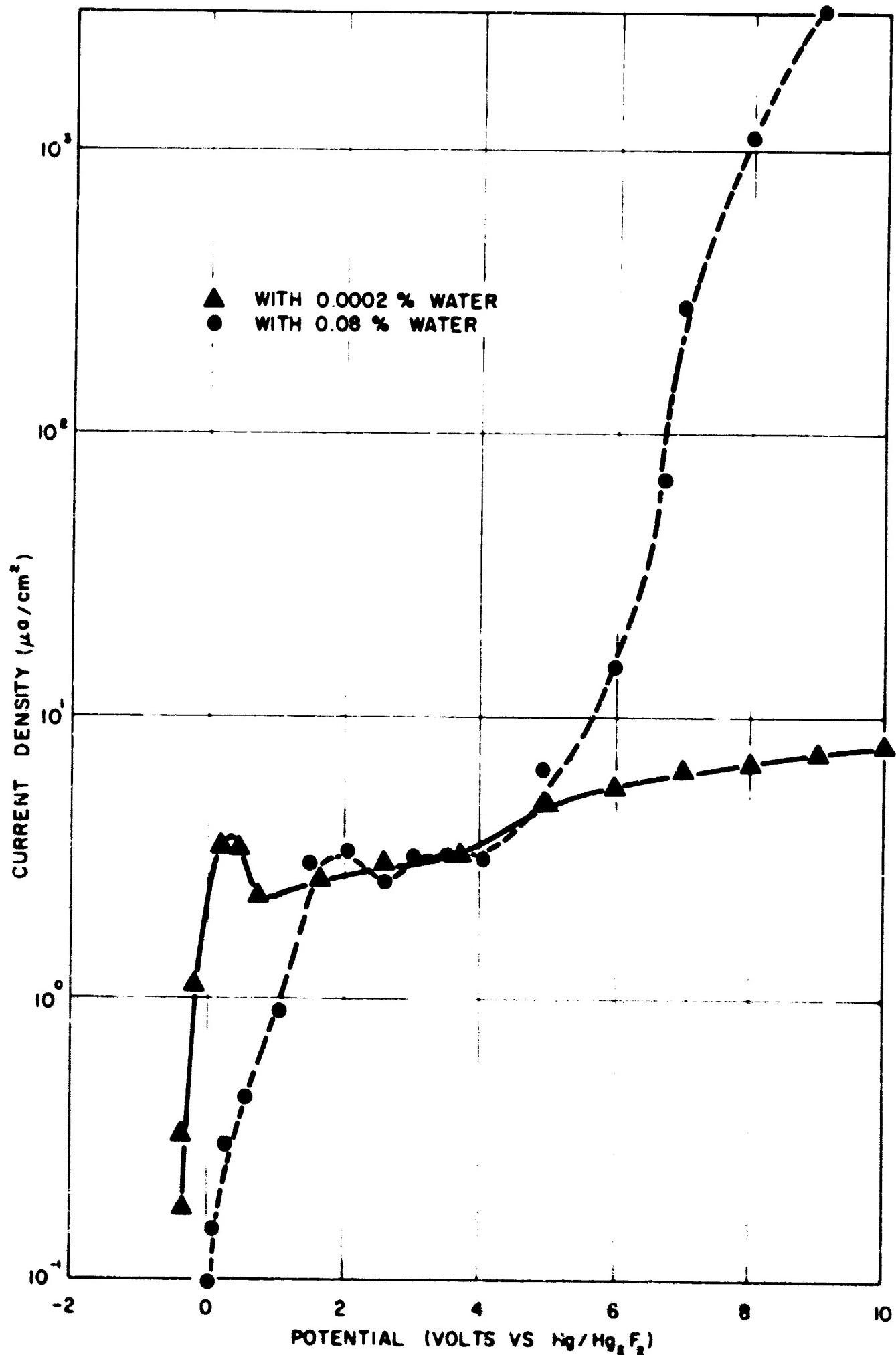


Fig. 9 - POLARIZATION CURVES FOR HASTELLOY-F IN AHF

Due to the high corrosion rates in AHF at the higher anodic potentials, and since fluorine could not be evolved from this electrode, Hastelloy-F cannot be used as an anode material, and no further work will be done using Hastelloy-F.

B. Cadmium

Weight loss studies were carried out on cadmium electrodes in AHF. The procedures used in cleaning and measuring the weight changes were the same as described for Hastelloy-F. The weight changes for times up to 16 hours with the electrode at open circuit are shown in Figure 10. The weight loss rate approached  $0.3 \text{ mg/cm}^2/\text{hr}$  at the end of the 16-hour period. Weight losses were much higher when the electrode was anodically biased at +2.0 v vs Hg/Hg<sub>2</sub>F<sub>2</sub>. After two hours at +2.0 v, a weight loss of  $153 \text{ mg/cm}^2$  was recorded, which compares favorably with  $125 \text{ mg/cm}^2$ , the calculated corrosion current weight loss.

Anodic polarization curves of cadmium in AHF with NaF (0.0125M) added are shown in Figure 11. The corrosion current completely dominates any other currents (e.g., F<sub>2</sub> evolution).

Due to its high corrosion rate in AHF, cadmium cannot be used as an anode material, and no further work is planned.

C. Zinc

Weight loss studies were carried out on zinc electrodes in AHF. Some difficulty was experienced in cleaning the electrode. No solvent was found that would dissolve the ZnF<sub>2</sub> film without also attacking the zinc. For this reason, the weight losses were calculated from the weight gains and these values were also plotted. Open-circuit weight losses for times up to 16 hours are shown in Figure 12. The loss rate approached  $0.134 \text{ mg}$  at the end of the 16-hour period.

Weight losses for anodically biased electrodes are shown in Figure 13. Weight loss rates for both potentials are of the same order of magnitude as the open-circuit rate.

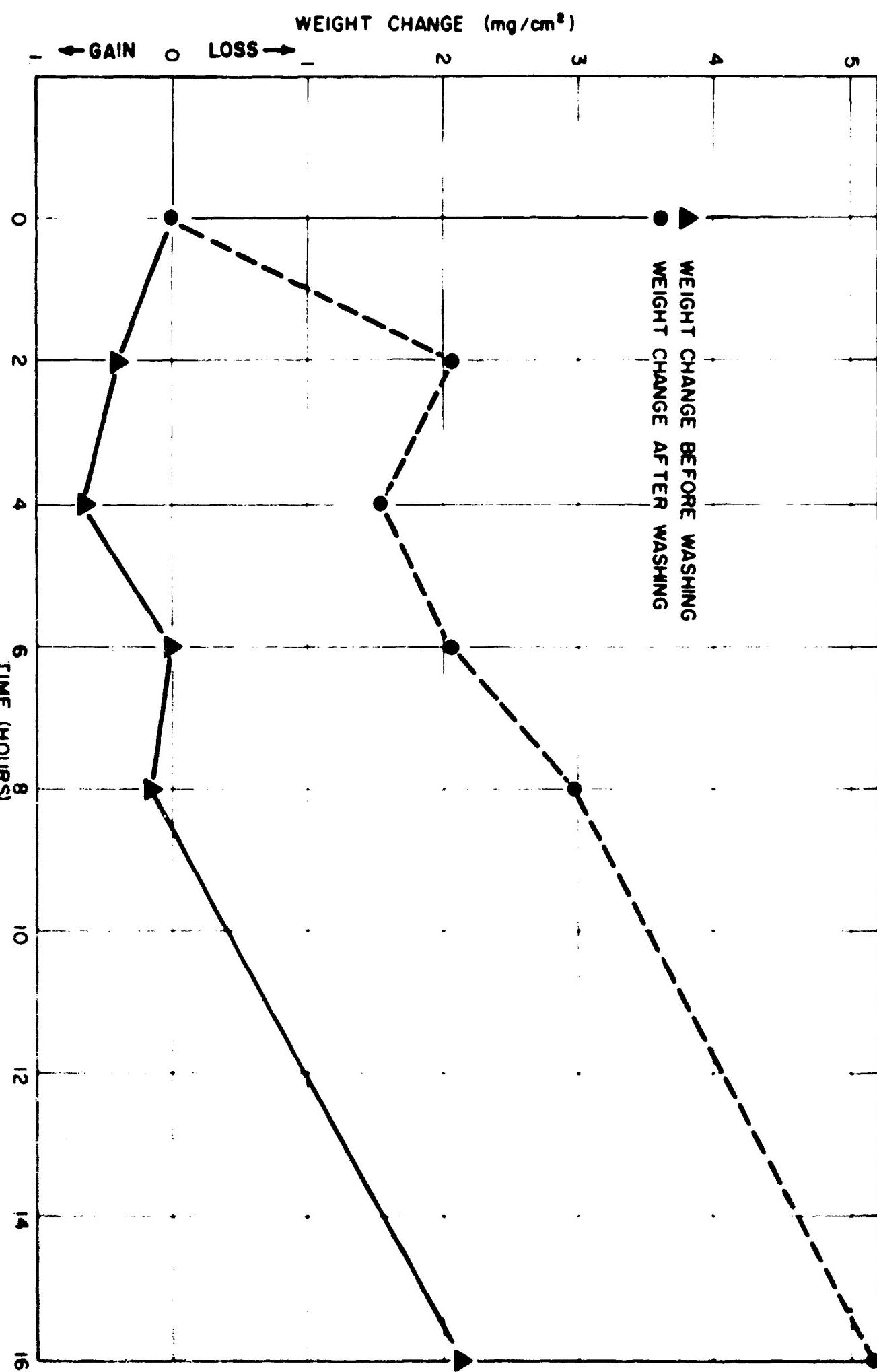


Fig. 10 - WEIGHT CHANGES OF CADMIUM IN AHF

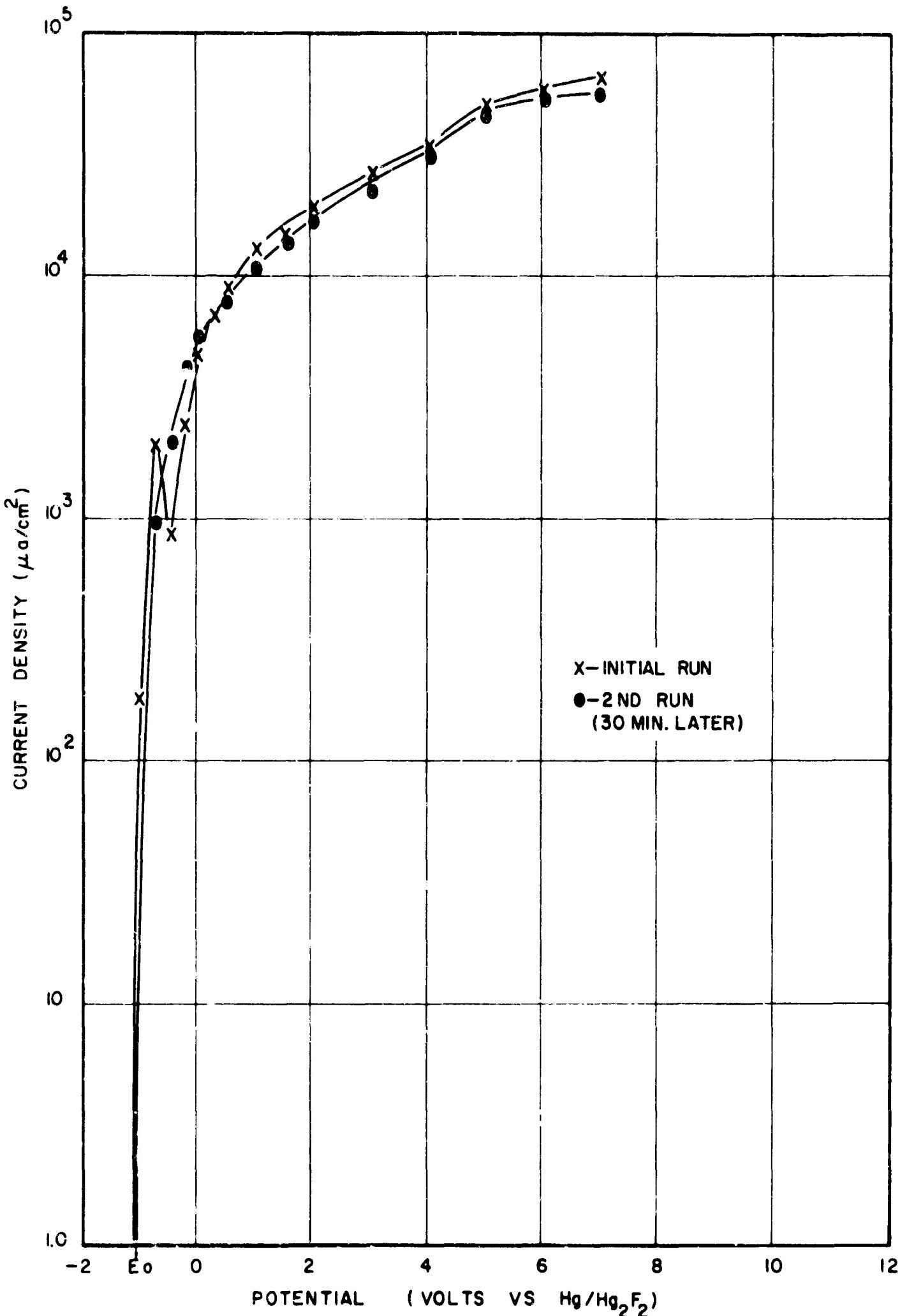


Fig.11 - ANODIC POLARIZATION OF CADMIUM  
IN 0.0125M  $\text{NaF}$  IN AHF

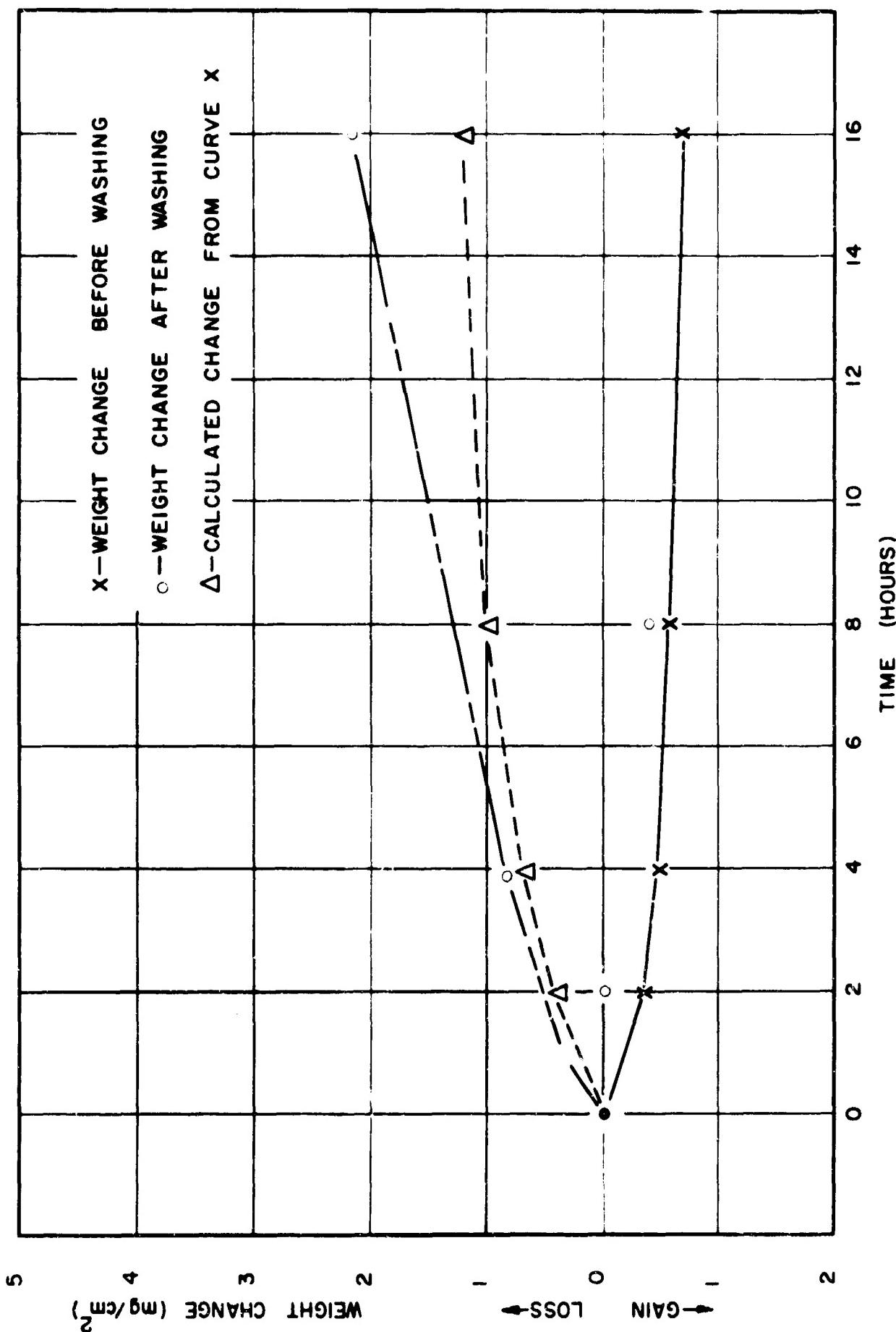


Fig. 12—WEIGHT CHANGES OF ZINC IN AHF AT OPEN CIRCUIT

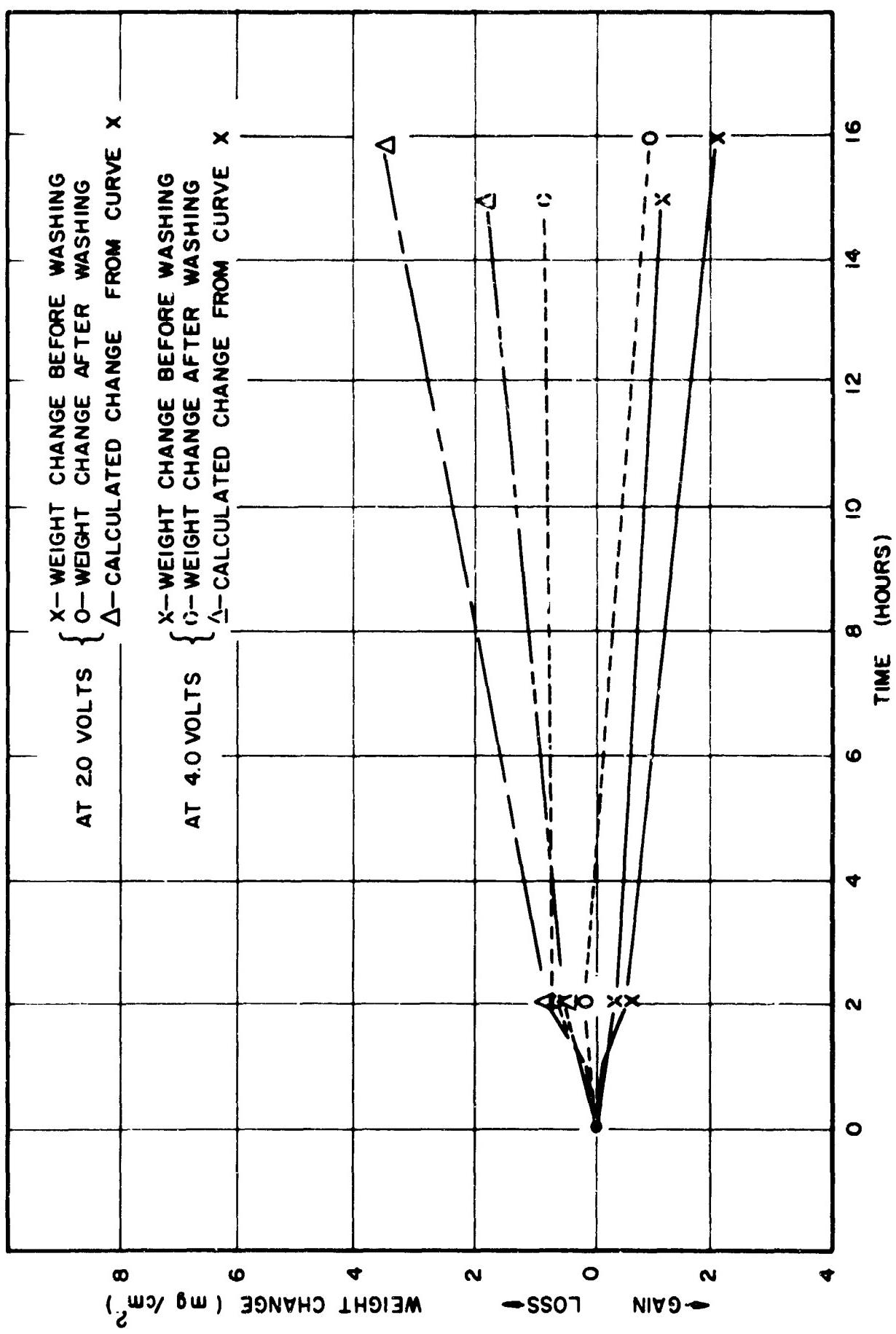


Fig. 13—WEIGHT CHANGES OF ZINC IN AHF AT ANODIC BIAS

Anodic polarization curves on zinc in AHF with and without NaF added are shown in Figure 14. After the initial run, the current density is quite low and no  $F_2$  evolution current is noted. This is probably due to the formation of a high resistance film during the initial run. No significant change in polarization characteristics was noted after addition of NaF (0.011M).

Due to the high corrosion rate of zinc in AHF, no further work is planned.

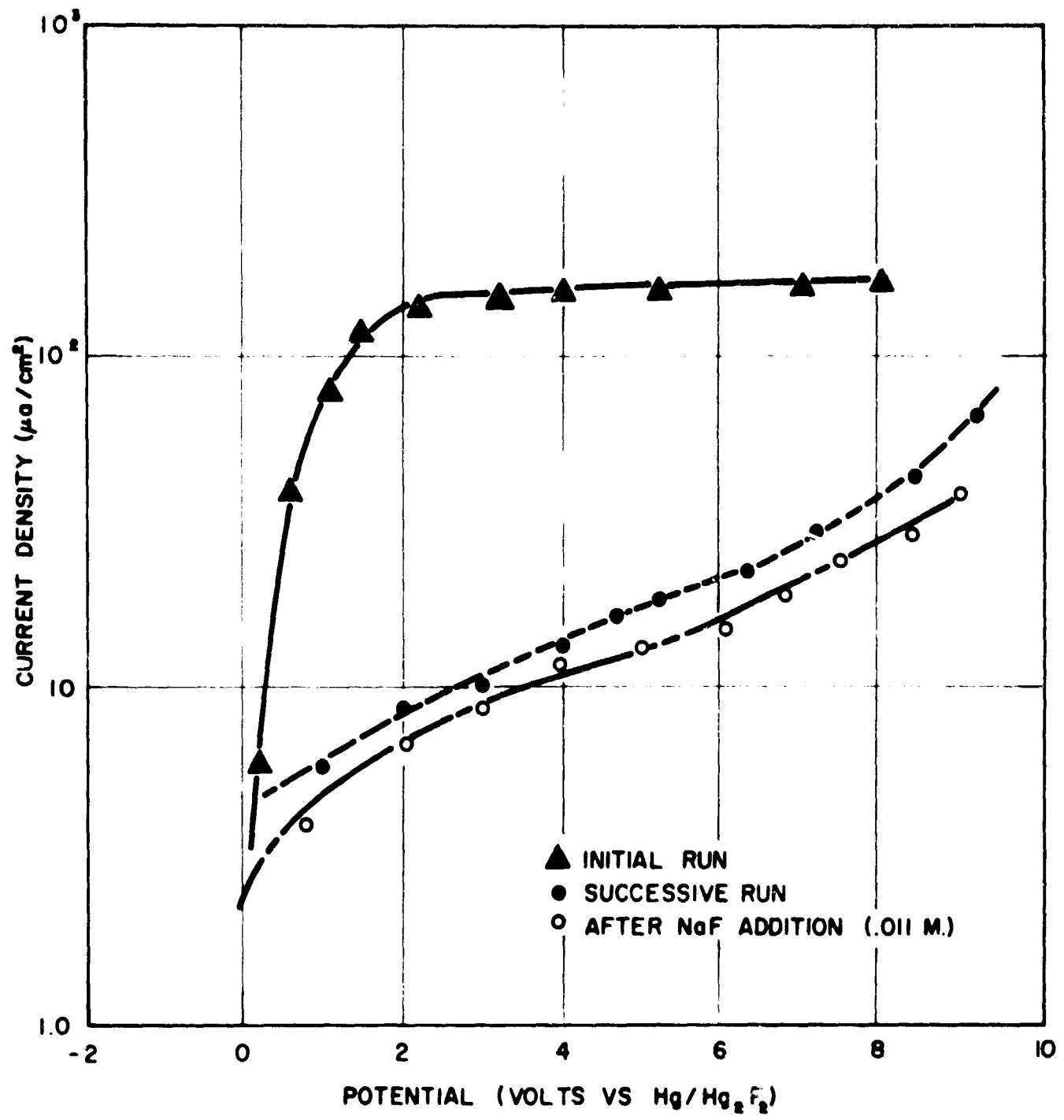


Fig. 14 - ANODIC POLARIZATION OF ZINC

VI. DISCUSSION

Results obtained to date show that a portion of the anodic current on Monel electrodes in AHF solutions of  $\text{NH}_4\text{F}$  goes to the formation of a permanent film. The data obtained indicate that the relative contribution of current to film formation is a small fraction of the total. Sufficient understanding of the electrode processes occurring has been achieved for an accurate measurement of the current involved in film formation. These data will be coupled with analyses of the products of electrolysis to give an overall description of the electrode processes that occur in the electrochemical fluorination of  $\text{NH}_4\text{F}$  solutions in AHF.

**VII. FUTURE WORK**

Work now in progress consists of further studies on the electrochemical fluorination of  $\text{NH}_4\text{F}$  in AHF. The character of the film on the Monel working electrode during the electrolysis of  $\text{NH}_4\text{F}$  is also being studied.

Further infrared and gas chromatography studies will be made as an aid in identifying the electrochemical fluorination products. A twenty foot, 1/4 inch Monel column, packed with #40 Kel-F grease on shredded Teflon, will be used on the gas chromatograph to get better separation of the electrolysis products.

Studies on the behavior of other electrode materials will also be continued.

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